# THE OXIDATION STATE OF GALLIUM IN Ga/HZSM-5 LIGHT ALKANE AROMATIZATION CATALYSTS

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ABSTRACT:

Gallium modified ZSM-5 catalysts were prepared and the transformations of propane were studied. The influences of catalyst pretreated with $H_2$ at different temperatures and addition of a small amount of $O_2$ and $H_2$ on propane aromatization were investigated. The reduction behavior and physical properties as well as the state and distribution of gallium species of the prepared catalysts were characterized by XPS, $H_2$-TPR and $NH_3$-TPD techniques. Considering the catalyst evaluation results and the characterization results, it was suggested that the gallium species existed as oxides and did not occupy the exchangeable ion position in the zeolite. Gallium oxides well dispersed on the zoelite and could be easily reduced might be the active species. It was suggested that the probable active oxidation state of gallium was less than +3 but greater than +1.

## 1.Introduction

Gallium modified HZSM-5 catalysts have been shown to exhibit increased activity and product selectivity for aromatizaton of light hydrocarbons such as propane and butane[1]. In recent years, much work has been done on the role of gallium species and the reaction mechanism. It has shown that gallium species is effective not only for dehydrocyclization of oligmers, but also for the direct dehydrogenation of alkanes to corresponding olefins. However the reactoin mechanism concerning gallium, especially about the active state of gallium remains unclear[1]. N.S.Gnep et al proposed $Ga^{+3}$ may be the active state, and the active species may be gallium oxide $Ga_2O_3$ highly dispersed in the zeolites[2]. By $H_2$-TPR study along with catalytic testing, G.L.Price et al came to the conclusion that the active species was probably $Ga^{+1}$ as a zeolitic cation and was not incorporated in the zeolite lattice[3]. Yuan et al also suggested that the higher aromatization activities were more likely to be related with the $Ga^{+1}$ species[4]. Further more, L.Petit et al had shown that at lower conversion level, $Ga_2O_3$ partially reduced by $H_2$ produced during propane aromatization had higher dehydrogenation activity than $Ga_2O_3$ that was further reduced at higher conversion level[5]. This suggested that the active valence of Ga should be less than +3.

According to our previous study, Ga neither entered into the zeolitic framework nor occupied any exchangeable cation position, it probably existed as highly dispersed $Ga_2O_3$ on the surface of HZSM-5[6]. A further study had shown that Ga components can be divided into two parts:active gallium species and free $Ga_2O_3$, the former having a strong surface interaction with HZSM-5. The active gallium species could be easily reduced by $H_2$ at lower temperatures[7].So it was difficult to determine the active valence of Ga in the reaction process since $H_2$ was one of the products.

In this paper, conversion of propane to aromatic hydrocarbons over Ga/HZSM-5 zeolite catalyst was tested as a model reaction. The influence of catalyst pretreatment with $H_2$ at different temperatures and the influences of $H_2$ and $O_2$ on propane conversion were studied. We report here our results about the active valence state of Ga in Ga/HZSM-5 catalysts.

## 2.Experimental

2.1 **Catalyst Preparation:** The catalyst Ga/HZSM-5 (I) was prepared by ion-exchange of HZSM-5 (with $SiO_2/Al_2O_3$ ratio about 56)with gallium nitrate solution. The obtained product then washed with water,dryed, and activated for 4hrs at 540 ℃ in air. The Ga/HZSM-5(M) was obtaoned by mixing HZSM-5 with gallium oxide, and then calcinated at 570 ℃ in air.

2.2 **Catalytic test:** propane aromatization reactions were carried out at atmospheric pressure in a microflow reactor using 1.2g catalyst. In all case, the concentration of propane in Ar was 20%

by volume, and in some other cases a small amount of oxygen or hydrogen was added in the feeding gas. Reaction temperatures were varied among 520-550 ℃. After 1h time on stream, the reaction products were analyzed by gas chromatography.

2.3 **Catalyst Characterization:** $NH_3$-TPD Method was used to measure the surface acidity of catalyst samples pretreated at different conditions[8]. XPS spectra were recorded with a PHI 5300 ESCA SYSTEM as in ref.7. TG technique was applied for the catalyst reduction process.

## 3. Results and discussion

### 3.1 Catalytic activity

As we had noticed before, the catalytic activity of propane conversion over Ga/HZSM-5 varied with catalyst pretreatment conditions. After the regeneration process, the conversion level changed compared to that of freshly activated catalyst. The activity leveled off upon several reaction regeneration performances. So in this paper, the catalyst had been subjected to several reaction-regeneration performances before the following data were obtained.

The catalytic reactions for propane aromatization were studied. Results shown that catalyst Ga/HZSM-5(I) had higher catalytic activity than Ga/HZSM-5(M) catalyst. Ga/HZSM-5 pretreated with various conditons were tested for propane conversion and the results are listed in table 1. Compared to the catalytic activity of the oxidized catalyst, the activity changed little with catalysts treated by 5% $H_2$ at 540 ℃ for 1h. Much activity decrease was obtained when the catalyst was reduced in 5% $H_2$ at 600 ℃ for 1h.The catalytic activity was largely restored after the catalyst was re-oxidized.

In order to obtain more information about the active state of gallium species, the effects of $O_2$ and $H_2$ addition to the feed on propane aromatization were also tested. The results are listed in table 2. As one can see in this table, a small amount of $O_2$ addition in the propane feed caused a suprising decrease of propane conversion and BTX selectivity. On the other hand, the influence of $H_2$ was small, the conversion of propane and the BTX selectivity changed slightly despite a higher yield of methane.

### 3.2 Characterization of the catalyst

Using IR technique, we had found that there was a little change of acidity before and after the introduction of gallium[9]. Here conventional $NH_3$-TPD method was applied to study the acidic properties of Ga/HZSM-5. Upon pretreatment by 5% $H_2$ at 540 ℃ for 1h, the total acidity did not change. Even pretreated at 600 ℃ the total acidity decreased only 3.2%, and most of acidic centers and their distribution remained unchanged. This further convinced that there was no exchange of Gallium with Bronsted acid site in the zeolite upon reduction at higher temperatures, and thus gallium existed as oxides dispersed into the zeolites.

Using TG technique, we calculated the Oxidation states of gallium, in the presence of $H_2$, up to 540 ℃ the oxidation state of Ga appeared to about +2, up to 600 ℃ less than +1.The results were inconsistent with that of G.L.Price[10]. The oxidation states of Ga before and after $H_2$ reduction were also studied by XPS technique. As one can see in fig. 1, after pretreatment in $H_2$ at 540 ℃, an additional peak appeared on the lower binding energy side of Ga 2p,which indicated that gallium species existed in several oxidation states. Because the reduced sample was stored for several days before XPS measurement, it was likely that the above result did not reflect the true oxidation state in the sample. Unfortunately we were not able to perform reduction experiment directly in the preparation chamber of the XPS device. However the XPS revealed that at least Ga/HZSM-5 can be reduced in 5% $H_2$. Since $H_2$ is one of the products in propane aromatization process, we propose that Ga species can be reduced during propane aromatization as was proposed by L.Petit[5].

### 3.3 The active state of gallium species

In the present investigation, our main aim is to determine the active state of gallium species that is still disputed in the literature. Considering the above results, we come to the following conclusions. As is known in the literature, acidic property of Ga/HZSM-5 catalysts is of great importance for propane aromatization. After the catalyst was pretreated at 600 ℃ in the presence of $H_2$, the acidity did not change much but the Ga oxidation state change to lower oxidation state less than +1. So in table 1 the activity decease can be attributed to the gallium state change. This is to say that lower oxidation state of Ga can not be the active state. If we assume the higher oxidation state be the active state, thus after the catalyst was pretreated in $H_2$, the

Table1. Aromatization of propane over Ga/HZSM-5 pretreated at different condition [a]

| No | Catalyst pretreatment[b] conditionb | $C_3^0$ conv. (%) | BTX yield (%) | Product selectivity(%) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | $C_1$ | $C_2$ | $C^=_3$ | $C_{4-7}$ | BTX |
| 1 | Oxidized at 540 ℃ | 43.3 | 31.4 | 7.8 | 9.7 | 7.1 | 2.7 | 72.6 |
| 2 | Reduced at 540 ℃ | 42.3 | 30.3 | 7.8 | 10.4 | 7.1 | 3.0 | 71.6 |
| 3 | Reduced at 600 ℃ | 32.8 | 22.0 | 7.6 | 12.5 | 8.8 | 3.9 | 67.1 |
| 4 | Re-0xidized at 540 | 40.6 | 29.5 | 8.4 | 9.7 | 6.4 | 2.9 | 72.6 |

a. Reaction temperature 535 ℃, WHSV of propane 1.84.

b. The catalyst was regenerated by air in Ar in all cases.

Table2. Effects of $O_2$ and $H_2$ on propane aromatization over Ga/HZSM-5[a]

| Composition of feed | | | | $C_3$ conv. | BTX yield | Product selectivity(%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| $C^0_3$ | Ar | $O_2$ | $H_2$ | (%) | (%) | $C_1$ | $C_2$ | $C^=_3$ | $C_{4-7}$ | BTX | COx |
| 20 | 80 | -- | -- | 60.3 | 43.2 | 9.8 | 9.9 | 5.3 | 3.4 | 71.6 | -- |
| 20 | 75.8 | 4.2 | -- | 48.0 | 27.8 | 9.4 | 11.1 | 6.6 | 2.2 | 57.9 | 12.9 |
| 20 | 72.5 | -- | 7.5 | 59.1 | 41.7 | 11.6 | 10.8 | 5.4 | 1.7 | 70.6 | -- |

a. Reaction temperature 545 ℃, WHSV of propane 2.0

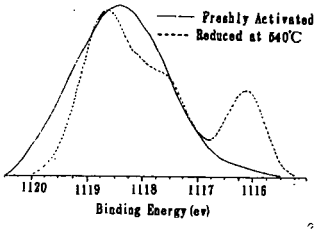


Fig.1 XPS spectra of Ga/HZSM-5 catalyst

catalytic activity would decrease due to the fact that the gallium was reduced to lower oxidation state. However this was not the case, after the catalyst was pretreated by 5%$H_2$ at 540 ℃ for 1h, the state of Ga changed, but the activity did not change much. Further more, the addition of a small amount of $O_2$ in the feeding gas caused a decrease of propane conversion level and the BTX selectivity also decreased. In theory, $O_2$ reacts with $H_2$ and thus accelerates the propane aromatization as in the case of using HZSM-5 as catalysts[11]; the negative effects on Ga modified HZSM-5 may due to the fact that presence of $O_2$ maintained Ga in its higher oxidation state. These results suggested that the higher oxidation state of Ga not be the active state.

With mild reduction at 540 ℃ for 1h, the activity did not change much compared to that of oxidized catalyst. Since in this case, Ga exists as +1 —+2, we presume that this should be the active valence state. This is further convinced by introducing a small amount of $H_2$ into the reaction system. The effect of $H_2$ on propane aromatization could be divided into two parts: on chemical equilibrium $H_2$ did not favor the propane conversion, but on the other hand, the presence of additional $H_2$ caused gallium in its active state; the first effect was balanced by the second one. So in this case, the activity did not change much.

Recently, P. Meriau deau et al[12] has studied the adsorption properties of $Ga_2O_3$ by FIIR technique,and found that with $H_2$ as adsorbate,the number of $Ga^{+y}$-H function group was higher when Ga was in +1 ~ +2 oxidation state.Our suggestion of gallium active state is strongly supported by Meriaudeau ' s findings.

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